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Deformation micromechanics in high-volume-fraction aramid/epoxy composites

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It is shown that Raman spectroscopy is an excellent technique for analysis of the relationship between structure and deformation processes in both high-performance fibres and fibre-reinforced composites. It is demonstrated that Raman spectroscopy can be used to follow molecular deformation processes in Kevlar 49 aramid fibres through stress-induced band shifts. The shift of Raman bands in a high-volume-fraction unidirectional composite is analysed and it is found that there are significant variations in local fibre strain due to imperfections in the composite microstructure. Furthermore, it is shown that it is possible to map the local fibre strain distributions around a hole in the composite. The distributions of axial fibre strain have also been mapped in both a plain weave and a four-harness satin weave Kevlar 49/epoxy composite. Complex distributions of local fibre strain that follow the pattern of the repeat units of the woven structures are found. The power of the Raman technique to follow composite micromechanics is therefore demonstrated.

(Keywords: aramid fibres; woven composites; Raman spectroscopy; stress concentrations; holes)

INTRODUCTION

It has been established by the author and co-workers over the past 10 years that Raman spectroscopy is an excellent method of following the micromechanics of deformation of aramid[1] and other[2-7] high-performance fibres. They have also demonstrated that Raman spectroscopy can be used to study the deformation micromechanics of high-performance fibres in model, single-fibre epoxy resin matrix composites[8-14].

Aromatic polyamide (aramid) fibres are now finding widespread use in a number of applications including ropes, cables, protective clothing and high-performance composites. The best-known materials are Kevlar®(Du Pont) and Twaron® (Akzo Nobel), which are both based on the poly(*p*-phenylene terephthalamide) molecule. By monitoring the peak position of the strain-sensitive $1610\,cm^{-1}$ aramid Raman band[1] it is possible to follow the deformation of the aramid fibres and to define the states of localized stress or strain in a composite matrix[8-14]. Furthermore, it has been shown that Raman spectroscopy is a powerful analytical technique that can be used to determine the local fibre stress or strain in conventional micromechanical test methods such as fragmentation[15] and single-fibre pull-out[13]. It is also possible to calculate the interfacial shear stress from the distribution of strain along the fibre using a simple balance of forces model[16].

This study describes the use of the Raman technique to map the distributions of fibre strain in high-volume-fraction unidirectional and woven aramid/epoxy composites. Following an investigation of the deformation of single aramid fibres, a detailed analysis is undertaken to determine the dependence of the local strain distributions in high-volume-fraction composites on the macroscopic level of strain. In particular, the distributions of fibre strain in unidirectional composites and the stress concentrations around a hole in the composite are investigated. The detailed periodic distribution of fibre strain along the piles in both plain weave and four-harness satin weave aramid/epoxy composites are also presented.

EXPERIMENTAL

Materials

The fibre used in this study was a commercial grade of aramid fibre, Kevlar 49. The fibres had been sized during processing to improve both the handling characteristics and matrix adhesion in composites. They had a diameter of $12\,\mu m$, a tensile modulus of $\sim$120 GPa, a tensile

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strength of ~2.6 GPa and a strain to failure of ~2.2%.

Two composite systems were investigated, both of which were supplied by Cytec Aerospace (Wrexham UK). The composites were cured under vacuum in an autoclave and their details are as follows[17].

1) Unidirectional one-ply composite consisting of ~62.5% of Kevlar 49 fibres in Cycom 753, an epoxy resin used extensively in marine applications. The composite was heated to 100°C at 5°C min^{-1} and the temperature was held at 100°C for 60 min.
2) Plain weave two-ply composite consisting of ~50% of Kevlar 49 fibres in Cycom 919, a toughened epoxy resin. The composite was heated to 120°C at 5°C min^{-1} and the temperature was held at 120°C for 90 min.
3) Four-harness satin weave one-ply composite consisting of ~50% of Kevlar 49 fibres in Cycom 919, a toughened epoxy resin, and processed in a similar way to the plain weave (2).

Raman spectroscopy

Raman spectra were obtained from the aramid fibres, both in air and within the composites, using a Spex double monochromator with the 632.8 nm red line of a 15 mW helium–neon laser focused through a modified Nikon microscope to a ~2 μm spot on the surface of the fibre. A highly-sensitive charge-coupled device (CDD) camera was used to collect Raman spectra using an exposure time of 7 s. The peak position of the strain-sensitive 1610 cm^{-1} Raman band[1,18] was used to map the fibre strains in the composites at various levels of applied strain.

SINGLE-FIBRE DEFORMATION

There are at least eight well-defined Raman bands in the full Raman spectrum obtained from Kevlar 49, most of which are found to shift under the application of stress or strain[18]. The strongest Raman band is at 1610 cm^{-1} and shifts significantly to lower wavenumber on the application of a tensile stress. It has been shown that there is an approximately linear shift in peak position with increasing strain and that the behaviour is very reproducible[17]. The rate of band shift per unit strain $d\Delta\nu/de = S$ for the Kevlar 49 fibres is $-4.83 \pm 0.17\,cm^{-1}$/% strain and the correlation coefficient is 0.9988 (ref. 17).

Rallis[17] has undertaken a detailed study of the statistics of the stress-induced band shifts in Kevlar 49 fibres. He took 80 measurements of the band peak position for a fibre strained to ~0.25%, both at the same position on the fibre and also randomly over a 20 mm length of fibre, using a spot size of the order of 2 μm in both cases. It was found that when the laser beam was focused on the same area of the fibre the standard deviation of the band peak position was very narrow (SD = 0.033 cm^{-1}) whereas, if the measurements were taken randomly over a 20 mm region, the distribution of peak positions was broader (SD = 0.061 cm^{-1}). This implies that there are imperfections in the fibres, such as a local variation of fibre diameter, although in both cases the distributions of Raman band peak position were relatively narrow.

Following the detailed analysis of the statistics of the Raman band positions at a constant strain, Rallis[17] looked at the development of broadening of the distribution of the 1610 cm^{-1} Raman band peak position (and hence local fibre strain) for Kevlar 49 during deformation. *Figure 1* shows the shift and broadening of the distributions of local fibre strain (determined from stress-induced band shifts) for 80 measurements taken at random over a 20 mm length of a fibre. It can be seen that there is a significant increase in the standard deviation of the strain, upon deformation up to 1.55% strain, that reflects a real spread in the local levels in the fibres, over and above any apparent spread due to random error in the measurement[17]. It is important to consider the origin of this behaviour. It is clearly a result of inhomogeneity in the deformation of the fibres, perhaps due to local variations in fibre structure and/or geometry.

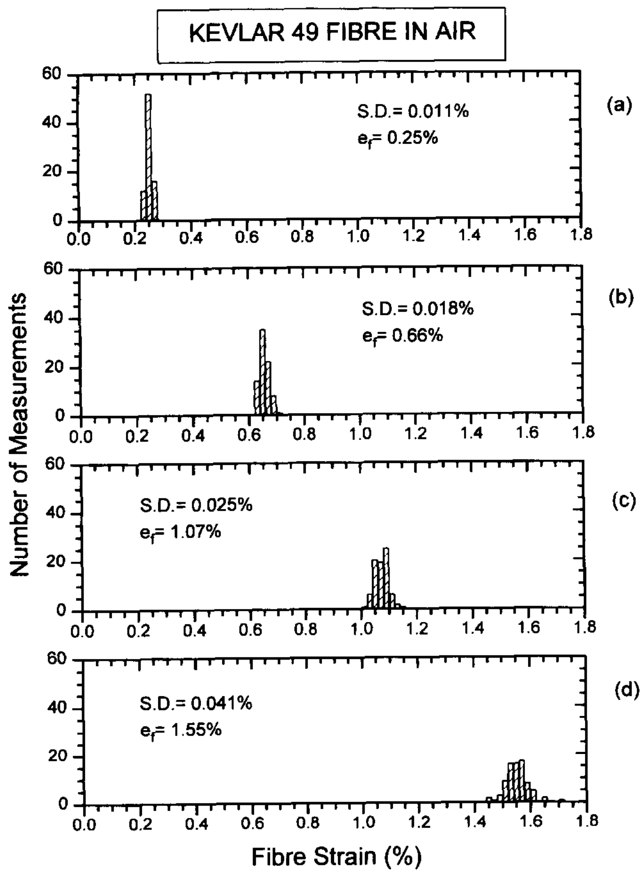

Figure 1 Histograms showing the local fibre strains determined from the 1610 cm^{-1} Raman band peak positions for a Kevlar 49 fibre subjected to increasing levels of strain (80 measurements obtained at random over a 20 mm region). Fibre strain: (a) 0.25%, (b) 0.66%, (c) 1.07%, (d) 1.55%

UNIDIRECTIONAL COMPOSITE

Local fibre strain

A series of measurements was undertaken of the local strains in the Kevlar 49 unidirectional composite subjected to axial deformation. In this case 200 measurements were obtained randomly at four different composite strain levels, e_c (determined using a resistance strain gauge attached to the specimen). The results are presented in the form of histograms in *Figure 2*. The first point to note is that there is an overall tensile (positive) strain in the fibres of the order of ~0.03% even when the composite strain e_c is zero. This may be due to a systematic error in the calibration of the zero-point of the band position, but it is more likely that it is due to residual stresses in the fibres induced during processing. Processing the composite by curing the resin at elevated temperature normally leads to compressive residual stresses in the fibres on cooling from the processing temperature[19]. This is because the thermal expansion coefficient of the epoxy resin matrix is usually significantly higher than that of the high-performance reinforcing fibres. In the present case, however, the residual strains are tensile and it appears that they were probably induced by stressing of the fibres during processing.

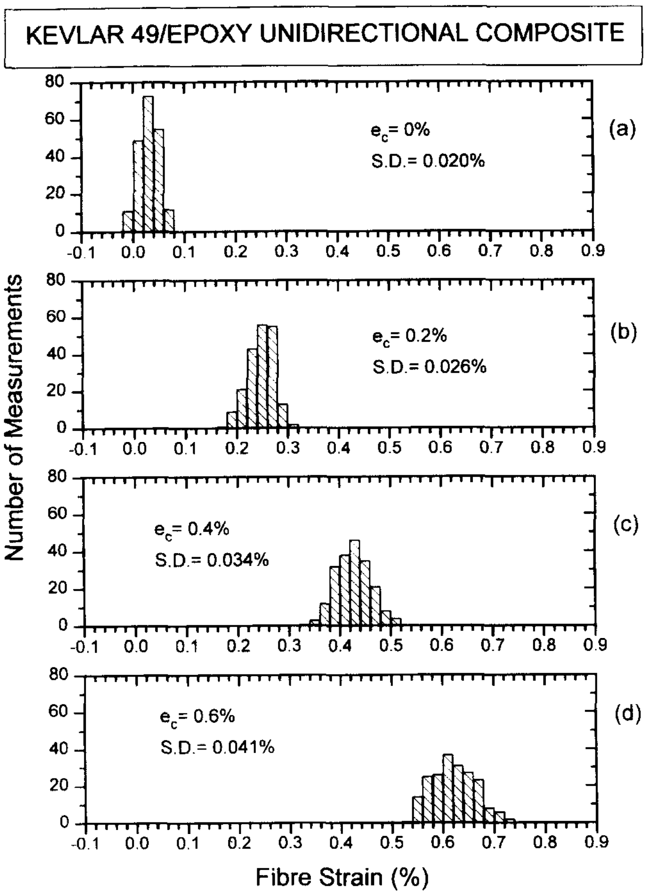

Figure 2 Histograms showing the local fibre strains determined from the 1610 cm^{-1} Raman band peak positions for a unidirectional Kelvar 49/epoxy composite subjected to increasing levels of strain (200 measurements obtained at random over the composite surface). Composite strain: (a) 0%, (b) 0.2%, (c) 0.4%, (d) 0.6%

It can be seen that axial stressing of the composite leads to tensile deformation of the fibres in the composite. Moreover, the average strain in the fibres is similar to the value of the composite strain e_c given by the strain gauge. What is most interesting, however, is that there is a spread of distribution of fibre strain that increases with increasing composite strain. This is significantly higher that the spread in the distribution of fibre strain that develops during the deformation of single fibres (*Figure 1*) and shows clearly that in the high-volume-fraction composite there is a large local variation of fibre strain.

Filiou and Galiotis[20–22] have undertaken similar studies using Raman spectroscopy to investigate the deformation of high-volume-fraction unidirectional P75 carbon/poly(ether ether ketone) (PEEK) composites. They found that there were relatively low levels of residual compressive strain in the P75 carbon fibres in the composites, of the order of −0.05%, which they demonstrated were similar to the values expected on cooling the composite from the processing temperature. The tensile fibre strain of the order of 0.03% found in the present study on the aramid/epoxy system is consistent with a tensile stress being applied to the fibres to aid processing. Filiou and Galiotis[21,22] also followed the tensile deformation of the fibres in a deformed P75/PEEK undirectional composite and found that there was a stress-induced band shift, indicating tensile deformation of the fibres. The average fibre strain followed the overall strain of the composite and it was found that the distribution of fibre strain broadened significantly following deformation as has been found in the present study. This broadening could be due to fibre fracture (particularly for the relatively brittle carbon fibres) but this is unlikely to be the case for aramids and is probably due to local imperfections in fibre orientation, packing density, etc.

Stress concentrations around a hole

In the next stage of the work, the variation of axial fibre strain was measured around a ~3 mm hole drilled in a 10 mm wide strip of the undirectional composite subjected to axial stressing. The hole was prepared using a 'Dixie' drill specially designed for drilling aramid composites while causing minimal damage to the edge of the hole. The distribution of the fibre strain around the hole in the composite subjected to a strain e_c of ~0.2% (measured using a strain gauge remote from the hole) was mapped by obtaining Raman spectra at different points. They were obtained at 200 μm intervals along rows 0.5 mm apart in the vicinity of the hole and at intervals of 400 μm further away from the hole. Measurements remote from the hole were taken in rows 1 mm apart. The findings are plotted in *Figure 3*, where the axial fibre strain can be determined from the intensity of the shading. It can be seen that the highest levels of axial fibre strain are in the vicinity of the equator of the hole (relative to the strain axis) and the lowest strains are at the meridian.

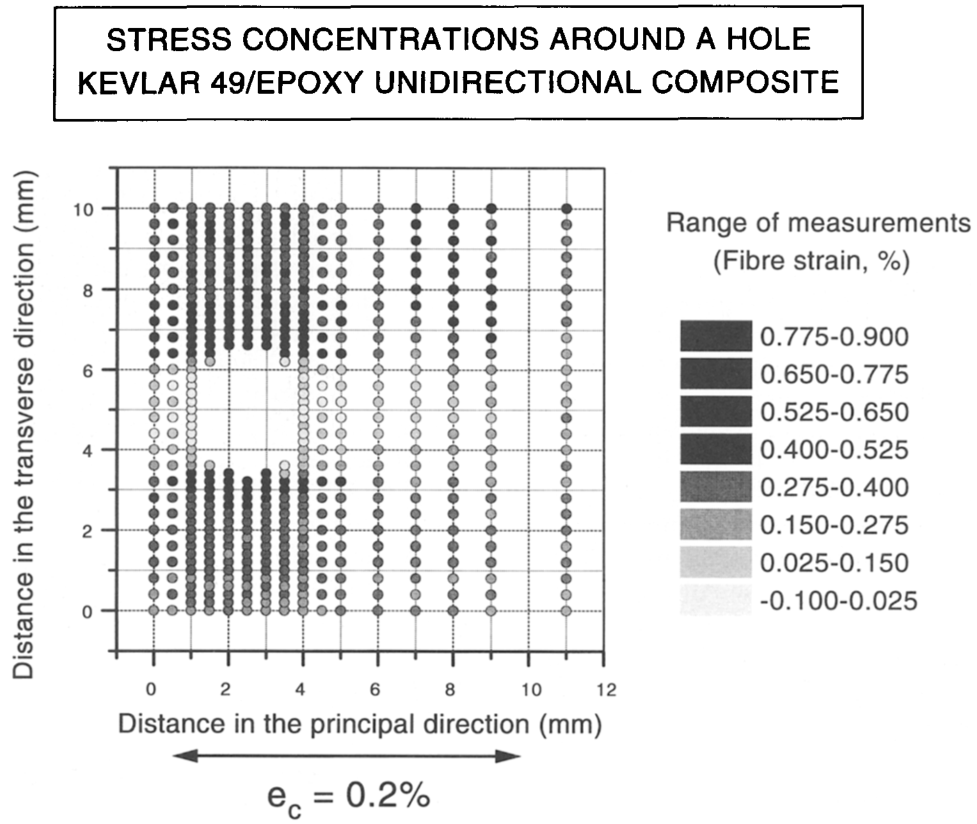

Figure 3 Distributions of axial fibre strain as a function of distance from a 3 mm hole in a unidirectional aramid/epoxy composite subject to an axial strain of 0.2%

This behaviour can be seen more clearly in *Figure 4*, which shows the variation of strain along the equator and meridian as a function of distance from the hole. The equatorial scan in *Figure 4a* shows that the strain is highest at the edge of the hole, showing a stress concentration of the order of 4. It then falls with distance away from the hole until it achieves a value of ~0.35% at the specimen edge, which is higher than the value of e_c measured remote from the hole. This is probably due to two reasons. First, it was shown earlier that there was a residual fibre strain of the order of 0.05% after processing, making the effective strain 0.25%. Secondly, since the size of the hole (~3 mm) is a significant proportion of the width of the specimen (10 mm), there will be an increase in the local fibre strain due to the reduction in cross-sectional area. This reduction in area will lead to an increase in strain by a factor of 10/7, i.e. from 0.25% to the 0.35% measured.

The meridional scan shown in *Figure 4b* is very different and shows that the axial fibre strain increases steadily with distance away from the hole to become slightly higher than the remote composite strain e_c. The strain at the edge of the hole must be zero since there can be no tensile stress perpendicular to a free surface. A small finite strain was measured, however, due probably to the difficulty in focusing in the damaged zone near to the edge of the hole.

The stress concentrations around circular openings in composite plates have been calculated by Greszczuk[23] for a variety of composite systems. In particular, he calculated the circumferential stress around a hole as a function of θ, the angle from the fibre axis, for unidirectional composites subjected to axial loading. For a glass/epoxy system it was shown that the stress concentration at the equator of the hole ($\theta = 90°$) is of the order of 4 and increases with fibre modulus such that it becomes about 9 for a graphite/epoxy composite. In this present study it was found that the stress concentration at the equator for the aramid/epoxy system (*Figure 4a*) was about 4, which is similar to that predicted for a glass/epoxy composite. The exact value of the stress concentration is difficult to measure using the Raman technique since it must be undertaken exactly at the edge of the hole where the fibres may be damaged. *Figure 4b* shows the variation of axial fibre strain as a function of distance from the hole at the meridian ($\theta = 0°$). It must be zero at the edge of the hole since the fibre axis is perpendicular to the free surface at this point. It can be seen from the figure that the strain increases from a low value at the edge of the hole to a value somewhat higher than e_c at a distance of 5 mm from the hole.

WOVEN COMPOSITES

Plain weave

An optical micrograph of the plain weave fabric used in the woven composite is shown in *Figure 5a*. The point-to-point variation of local fibre deformation was determined for the woven composite using strain-induced

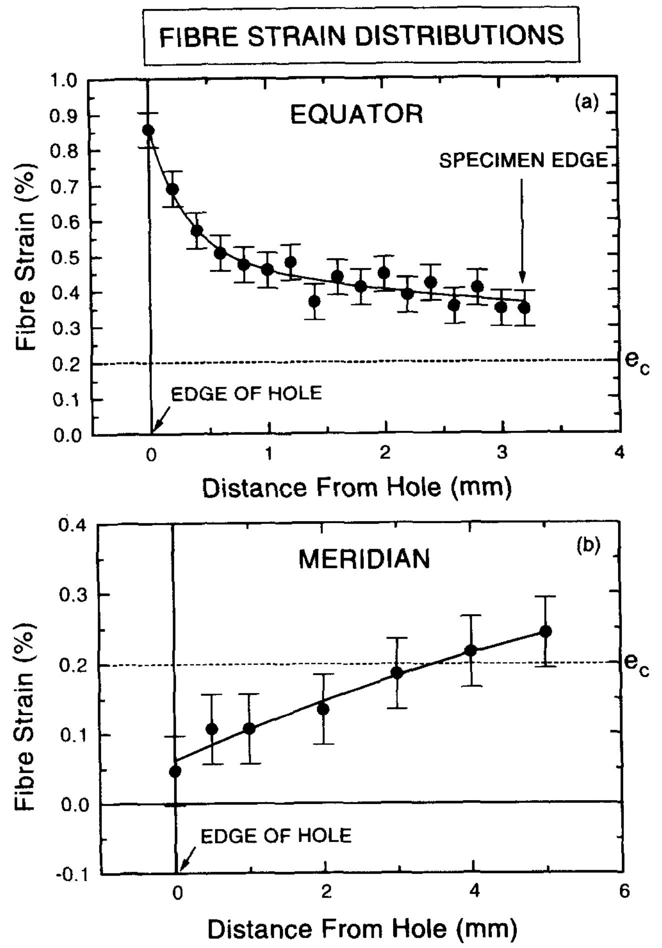

Figure 4 Distributions of axial fibre strain around a 3 mm hole in a unidirectional aramid/epoxy composite subjected to an axial strain of 0.2% in the horizontal direction. (a) Strain along the equator as a function of distance from the hole; (b) strain along the meridian as a function of distance from the hole

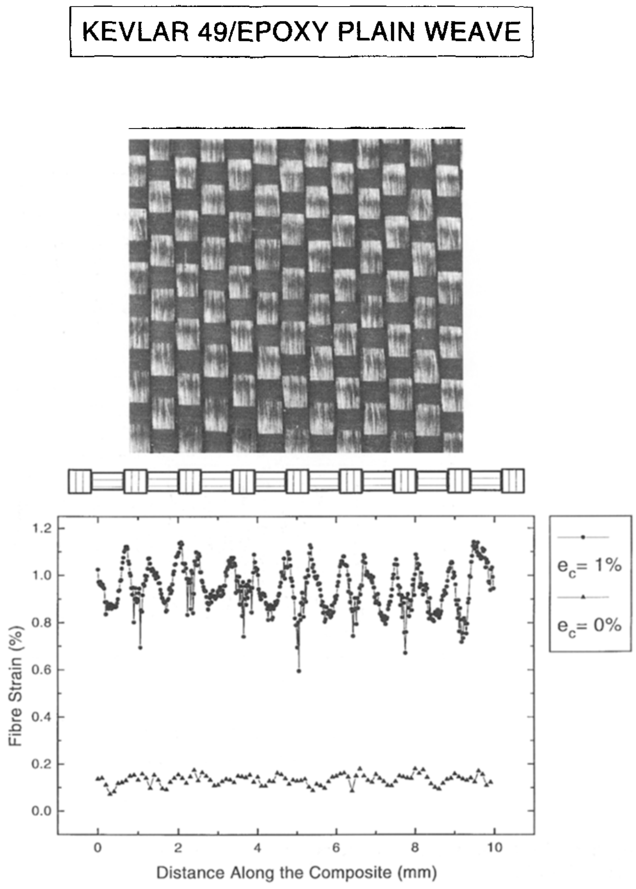

Figure 5 Kevlar/epoxy plain weave composite. (a) Optical micrograph of the fabric used in the composite; (b) variation of axial fibre strain with distance along the centre of the repeat pattern, at two levels of composite strain in the horizontal direction

Raman band shifts from the fibres in the composites subjected to axial deformation in the horizontal direction. This was done by first of all taking a series of Raman spectra at 20 μm intervals along the centre of a tow of fibres lying in the horizontal direction in *Figure 5a*.

Figure 5b shows the derived variation of fibre strain along a horizontal tow of fibres in *Figure 5a*. At a composite strain of 0% (i.e. undeformed) the fibre strain is of the order of 0.1%, which may be due to stresses induced during fabrication. A sketch of the weave pattern is also given in the figure and can be seen that the distribution of fibre strain at a composite strain of 1% follows that pattern of the weave very closely. It can be seen that where the horizontal fibres are at the surface the axial fibre strain averages about 1%, although it is highest where the fibres emerge from under the crossing fibres, and is a minimum in the centre of this region. Values of strain are also given in *Figure 5b* for the crossing fibres even though they are perpendicular to the straining direction and the direction of polarization of the laser beam. The Raman signal from such fibres is very weak and so the data are rather scattered. Nevertheless, it shows that the crossing fibres are subjected to an axial strain of about 0.8%.

Four-harness satin weave

An optical micrograph of the four-harness satin weave fabric used in the woven composite is shown in *Figure 6a*. The point-to-point variation of local fibre deformation was again determined for this woven composite using strain-induced Raman band shifts from the fibres in the composites subjected to axial deformation in the horizontal direction. This was done by taking a series of Raman spectra at 50 μm intervals along the centre of a tow of fibres lying in the horizontal direction in *Figure 6a*.

Figure 6b shows the derived variation of fibre strain along the horizontal fibres in *Figure 6a*. At a composite strain of 0% (i.e. undeformed) the fibres are virtually unstrained, indicating that in this composite the thermal stresses are very low. From the sketch of the weave pattern it can be seen that the distribution of the fibre strain again follows the pattern of the weave very closely. In this case 3/4 of the fibres appear on the surface and they are subject to a variable strain of the order of 1% at $e_c = 1\%$, although it is high where the fibres emerge from under the crossing fibres but is a maximum in the centre of this region. Values of strain are again given in *Figure 6b* for the crossing fibres perpendicular to the straining direction and the direction of polarization of the laser bean. This again shows that the crossing fibres are

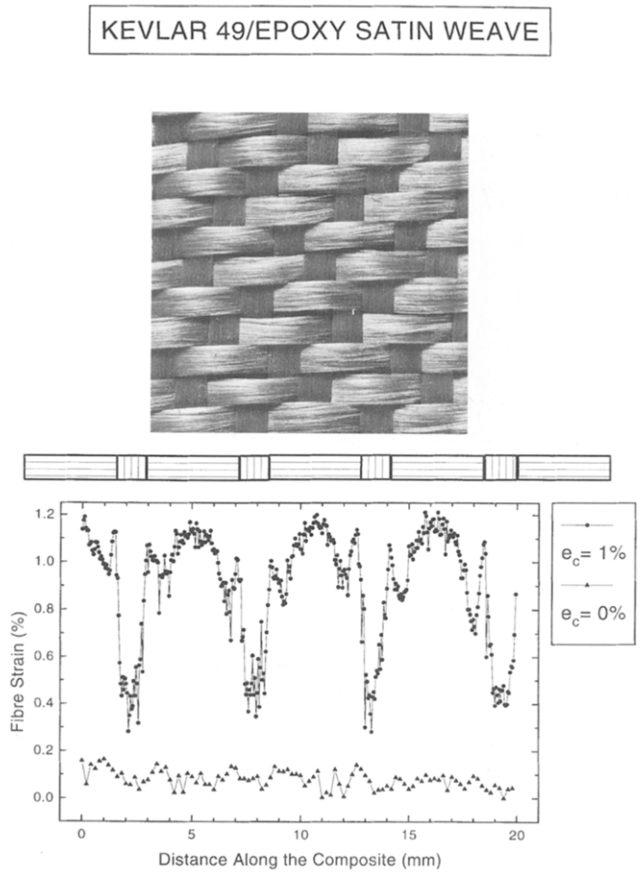

Figure 6 Kevlar/epoxy four-harness satin weave composite. (a) Optical micrograph of the fabric used in the composite; (b) variation of axial fibre strain with distance along the centre of the repeat pattern, at two levels of composite strain in the horizontal direction

subjected to an axial strain of between 0.2% and 0.7% and there is also a definite repeating pattern in the distribution of fibre strain in the crossing fibres.

The patterns of fibre strain in *Figures 5b* and *6b* give a unique insight into the fibre stress and strain distributions in woven composites structures. Unfortunately there is a lack of literature on the micromechanics of woven composites. The most detailed review has been undertaken by Chou[24] but most reports are concerned only with the mechanics of woven composite structures. It is hoped that in the future findings from this present study could be combined with modelling of the behaviour of woven composites, so that the behaviour of these important materials can be better understood.

CONCLUSIONS

It is clear that Raman spectroscopy is a powerful technique to follow deformation processes in aramid fibres and composites. It has been shown that there are variations of the strain in individual fibres in a deformed high-volume-fraction uniaxially aligned Kevlar 49/epoxy composite due to local imperfections in the composite structure. The use of the Raman technique to map fibre strain around holes in unidirectional composites has also been demonstrated and the values of stress concentration found are in line with theoretical predictions. One of the most interesting findings has been that it is possible to map of the point-to-point variation of fibre strain in woven composites, where it has been found that the patterns of fibre strain follow closely the repeat units of the woven structures. This shows that the technique has considerable potential in being able to map the local fibre deformation in such complex structures and offers the possibility of being able to analyse the detailed deformation micromechanics in such systems.

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